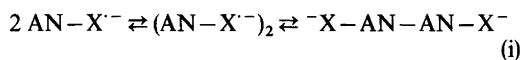


The Kinetics and Mechanism of the Reversible Dimerization of Anthracene Anion Radicals Substituted with Electron Withdrawing Substituents

OLE HAMMERICH^a and VERNON D. PARKER^b

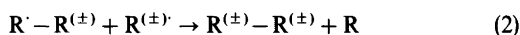
^a Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK 2100, Copenhagen, Denmark and ^b Institute for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Anthracene anion radicals substituted in the 9-position with nitro, formyl or cyano undergo dimerization in DMF to form stable dianions. Although the equilibria favor the dimers, the reverse reaction could be detected by linear sweep voltammetry at low sweep rates. Derivative cyclic voltammetry coupled with linear sweep voltammetry was used to establish that the reaction order in anion radical in the forward step is equal to 2 and that the substrate is not involved in the dimerization. The observed rate constants were unchanged when residual water was removed by conducting kinetic studies in solvent over neutral alumina, thus showing that water is not involved in the dimer forming reactions. Variable temperature studies showed that the apparent rate constants are nearly independent of temperature which rules out a simple dimerization mechanism. Since the observed rate law, $\text{rate} = k_{\text{obs}}[\text{AN}-\text{X}^{\cdot-}]^2$ contains only the anion radical concentration the complication is proposed to be the reversible formation of a dimer complex prior to forming the dimer dianion according to (i), with the first equilibrium showing



an inverse temperature effect.

The mechanisms of dimer forming reactions of ion radicals have recently been brought into sharp focus by the conclusive demonstration that some olefinic ion radicals take part, predominantly, in the ion radical–substrate coupling mechanism (eqns. 1 and 2).^{1–3} The first established case of this



mechanism involves the 4,4'-dimethoxystilbene cation radical¹ which had previously been proposed to undergo a simple dimerization mechanism.^{4,5} Even more interesting is the revelation that the favored mode of electrohydrodimerization of activated olefins is also the anion radical–substrate coupling reaction, providing that proton donors are effectively removed from the solvent–electrolyte systems.^{2,3} A large number of papers had previously been published on the mechanism of the latter reaction and the general conclusion resulting from those studies was that the key step in the reactions is the dimerization of anion radicals (eqn. 3).^{6–10}



Since the foundations of the conclusions on which the accepted mechanisms of electrodimersation have been demolished by the recent^{1–3} studies, we were curious to know if the simple radical–radical dimerization ever occurs in the ion radical series. A likely possibility to demonstrate this mechanism appeared to be for the dimer forming reactions of 9-nitroanthracene anion radical¹¹ and related substituted anthracenes.¹² These anion radicals have been observed to form stable dianion dimers and it seemed unlikely that proton donors could be involved in the reactions, leaving the dimerization

and the ion radical–substrate mechanisms as the apparent possibilities.

Voltammetric studies of the reduction of the 9-substituted anthracenes indicated that the dimer forming reaction is rapid and that the dimer dianions are oxidized at potentials about 500–1,000 mV more positive than the reduction peak due to the substrate. The voltammetry of 9-cyanoanthracene indicated that the formation of the dimer dianion from the anion radical is a reversible process. The evidence for this was that the peak current ratio of cyclic voltammograms approached unity as the sweep rate was decreased. The reversibility was also shown by ESR spectroscopy which indicated that measurable concentrations of the anion radical are present in solutions of the dimer dianion. Thus, the conclusion was drawn that the oxidation current due to the anion radical was a consequence of the dissociation of the dimer dianion, the rate of which is rapid relative to the low sweep rates employed. No attempts were made to “out-run” the dimerization step at high sweep rates.¹²

Thus, the available evidence suggested that the reduction of AN–X, where X is an electron withdrawing substituent, is accompanied by a reversible dimerization of the anion radical. It was the object of this study to show that this is indeed the case.

RESULTS

Derivative cyclic voltammetric mechanism analysis.

If the rate of reactions following electron transfer at an electrode are sufficiently slow that the primary intermediate can be observed by cyclic voltammetry, the mechanism can be determined using linear relationships recently described.¹³ The analysis involves eqn. (4) where R'_1 is the ratio of the maxima

$$\ln R'_1 = m \ln(1/\nu) + c \quad (4)$$

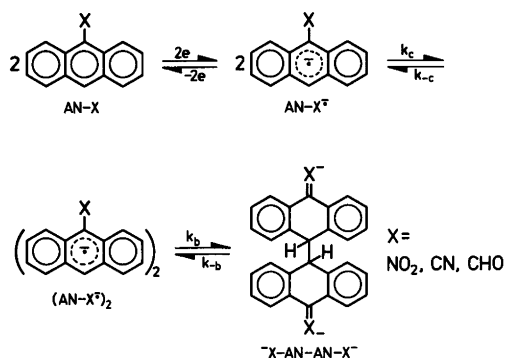
on the derivative of the backward and forward scans of the cyclic voltammogram and ν is the voltage sweep rate. The correlation parameters, m and c , are derived from theoretical data and are dependent upon the mechanism of the electrode process. The value of m when the switching potential is 300 mV beyond the reversible potential is -0.307 for the simple dimerization and -0.319 for the radical–substrate with rate determining electron transfer mechanism.¹³ Thus, the analysis does not

distinguish between these two possibilities but if either of the mechanisms are involved in a process, the experimental m value would be expected to be within experimental error, or about 0.01, of the theoretical values. The analysis is demonstrated for the reduction of the anthracenes substituted with electron withdrawing groups in Table 1. The region of data where (4) applies is limited to R'_1 ranging from about 0.25 to 0.75. The values of m found were -0.264 for AN–NO₂ and -0.268 for AN–CHO, both at a concentration of 1.00 mM, and -0.219 for AN–CN when the concentration was 0.40 mM. These data rather conclusively rule out the simple dimerization or the ion radical–substrate coupling schemes.

Table 1. Derivative cyclic voltammetric mechanism analysis of the dimerization of 9-substituted anthracene anion radicals in DMF.^a

$\nu/V \text{ s}^{-1}$	$R'_1{}^c$
9-Nitro (1.00 mM) ^b	
10.0	0.201(0.001)
20.0	0.226(0.003)
40.0	0.271(0.001)
80.0	0.328(0.001)
120	0.360(0.001)
200	0.417(0.003)
$d \ln R'_1/d \ln(1/\nu)$	-0.264
9-Formyl (1.00 mM)	
10.0	0.272(0.005)
20.0	0.320(0.004)
40.0	0.393(0.008)
80.0	0.482(0.004)
120	0.526(0.005)
200	0.607(0.006)
$d \ln R'_1/d \ln(1/\nu)$	-0.268
9-Cyano (0.40 mM)	
20.0	0.560(0.013)
40.0	0.665(0.012)
60.0	0.724(0.006)
80.0	0.755(0.009)
$d \ln R'_1/d \ln(1/\nu)$	-0.219

^a Measurements according to Ref. 13 in solvent containing Bu₄NBF₄ (0.1 M) at a mercury electrode at 22 °C. ^b 9-Substituted anthracene. ^c The ratio of the peaks on the backward and forward CV scans.



Scheme 1.

Preliminary experiments indicated that plots of R'_i versus ν show a decreasing trend with decreasing sweep rate, as expected, but go through a minimum value and increase again at lower sweep rates. This unusual behaviour indicates that all of the reactions are reversible as previously¹² suggested only for the reaction of $\text{AN}-\text{CN}^{\cdot-}$. Data for all three substrates are summarized in Table 2. The minima are observed in all cases at a sweep rate of about 1 V s^{-1} .

The DCV data indicate that the behaviour of the three substrates is qualitatively the same but that the rates of the overall processes depend upon the substituent, decreasing in the order; 9-nitro > 9-formyl > 9-cyano.

Linear sweep voltammetric mechanism analysis. Preliminary experiments indicated that the peak potentials during the reduction of 9-cyanoanthracene are nearly independent of ν in the range 100–

1000 mV s^{-1} . Likewise, during the reduction of 9-nitro and 9-formylanthracene the peak potentials did not shift linearly with $\log \nu$ at sweep rates lower than about 200 mV s^{-1} . Thus, the analysis is not applicable to study the 9-cyano compound and a limited range of ν could be applied to the reductions of the other two substrates. Data obtained with ν ranging from $200-1000 \text{ mV s}^{-1}$ are summarized in Table 3. The precision in the peak potential measurements, of the order of $\pm 0.2 \text{ mV}$, allowed the slopes to be obtained in spite of the narrow range of ν . Values of 18.3 ± 0.5 and -17.8 ± 0.6 were observed for $dE^p/d \log \nu$ and $dE^p/d \log C_A$, respectively, for 9-nitroanthracene. The corresponding values when the substrate was 9-formylanthracene were found to be 17.8 ± 1.5 and $-17.6 \pm 1.2 \text{ mV/decade}$.

The slopes can be predicted¹⁴ from eqns. (5) and (6) where A indicates the substrate and $a, b,$

$$dE^p/d \log \nu = (1/(b+1))RT/F \quad (5)$$

$$-dE^p/d \log C_A = ((a+b+i-1)/(b+1))RT/F \quad (6)$$

and i are reaction orders in substrate, ion radical, and any species formed during the reaction which further participate. The simple dimerization mechanism is described by rate law (7) while rate law (8) is for the ion radical–substrate coupling mechanism where electron transfer, analogous to (2) is

$$\text{Rate} = k_{\text{obs}}[\text{AN}-\text{X}^{\cdot-}]^2 \quad (7)$$

$$\text{Rate} = k_{\text{obs}}[\text{AN}-\text{X}^{\cdot-}]^2[\text{AN}-\text{X}] \quad (8)$$

Table 2. Derivative cyclic voltammetry studies at low sweep rates during the dimerization of substituted anthracene anion radicals in DMF.^a

$\nu/\text{V s}^{-1}$	R'_i for anthracene substituted with		
	9-Nitro (1.00 mM)	9-Formyl (1.00 mM)	9-Cyano (0.40 mM)
0.020	0.278(0.002)	0.277(0.014)	—
0.040	0.244(0.005)	0.239(0.004)	—
0.070	0.221(0.002)	0.218(0.010)	—
0.100	0.208(0.003)	0.210(0.001)	0.693(0.002)
0.200	0.181(0.001)	0.184(0.001)	0.589(0.002)
0.400	0.168(0.000)	0.174(0.000)	0.529(0.002)
1.00	0.157(0.001)	0.178(0.000)	0.453(0.003)
4.00	—	—	0.487(0.001)

^aFor conditions see Table 1.

Table 3. Linear sweep voltammetry mechanism analysis of the dimerization of 9-substituted anthracene anion radicals.^a

Substituent	[Substrate]/mM $v/V s^{-1}$	$-E^p/mV^b$			$dE^p/d \log v^c$
		0.200	0.400	1.000	
9-Nitro	0.20	376.3(0.3)	382.2(0.2)	389.2(0.3)	18.4
9-Nitro	0.40	371.2(0.1)	376.2(0.1)	383.6(0.0)	17.8
9-Nitro	1.20	362.0(0.2)	367.6(0.1)	375.3(0.2)	19.0
9-Nitro	2.00	359.3(0.1)	363.8(0.1)	371.9(0.1)	18.1
	$dE^p/d \log C_{NO_2}^c$	-17.5	-18.4	-17.4	
9-Formyl	0.20	422.9(0.2)	428.3(0.2)	434.3(0.2)	16.2
9-Formyl	0.40	417.4(0.2)	422.7(0.1)	429.8(0.1)	17.7
9-Formyl	0.80	411.7(0.1)	417.5(0.1)	424.0(0.0)	17.5
9-Formyl	2.00	404.0(0.0)	410.8(0.0)	418.0(0.1)	19.9
	$dE^p/d \log C_{CHO}^c$	-18.9	-17.5	-16.5	

^a For conditions see Table 1. ^b Measured by derivative LSV with potentiostat bias settings of -1.00 and $-1.20 V$ vs. Ag/Ag^+ in acetonitrile for the nitro and formyl substituted compounds, respectively. The numbers in parentheses are the standard deviations in 5 replicates. ^c In mV/decade. The subscripts identify the substituent.

rate determining. Application of (5) and (6), where i is 0, on these two rate laws leads to the predictions that both slopes should be $(1/3)RT/F$ for the simple dimerization mechanism while $dE^p/d \log v$ is predicted to be $(1/3)RT/F$ and $dE^p/d \log C_A$ is predicted to equal $-(2/3)RT/F$ for the radical-substrate coupling mechanism.

The LSV results are consistent with the simple dimerization and clearly inconsistent with the ion radical-substrate coupling mechanism. The fact that the slopes are slightly lower than the theoretical value, 19.5 mV/decade at 295 K, is most likely due to the complication observed at lower sweep rates involving the dissociation of the dimer.

Reaction order analysis. A general method for determining reaction orders of electrode processes even when the mechanism is unknown has recently been described.¹⁵ The method is based upon eqn. (9), for the case when DCV is the measurement technique, which shows that R'_1 is a function of the apparent rate constant (k_{app}), the substrate concentration to the a power and the reciprocal of the voltage sweep rate, providing that all other parameters are held constant. Thus, if R'_1 is held constant

$$R'_1 = f[k_{app} C_A^a (1/v)] \quad (9)$$

by appropriate variations in v while C_A is varied, the changes necessary in v directly give the changes

in the rate brought about by the concentration changes. For the simple dimerization reaction v_c/C_A , where the subscript c indicates the value of the sweep rate

Table 4. The effect of substrate concentration on the rate of dimerization of substituted anthracene anion radicals in DMF.^a

[Substrate]/mM	$v_3/V s^{-1}$	$k_{app}/M^{-1} s^{-1} b$
9-Formyl		
0.25	17.1	3.12×10^5
0.50	34.0	3.10×10^5
1.00	66.0	3.01×10^5
2.00	106	2.42×10^5
9-Nitro		
0.25	82.0	1.50×10^6
0.50	175	1.59×10^6
9-Cyano		
0.25	12.5 ^c	1.26×10^5
0.50	25.8 ^c	1.30×10^5
1.00	52.5 ^c	1.32×10^5
2.00	110 ^c	1.39×10^5

^a See Table 1 for the conditions. ^b Calculated assuming a simple dimerization mechanism from, $k_{app} = 4.57 v_3/C_A$ where C_A is the substrate concentration, according to Ref. 15. ^c The voltage sweep rate when $R'_1 = 0.600$.

necessary to hold R_i' constant, is predicted to be constant reflecting the fact that the reaction is second order in anion radical.

The data in Table 4 show that the relationship described in the previous paragraph holds reasonably well for the reduction of all three substrates. The value of v_c , $v_{1/2}$ for AN-NO₂ and AN-CHO, and $v_{0.6}$ for AN-CN, is very nearly proportional to the concentration of the substrates. The last column in the table gives k_{app} values which were calculated assuming the simple dimerization mechanism. These values are only given for comparison purposes since it is clear from the DCV data in Table 1 that the simple dimerization mechanism does not describe the dimer forming reactions of the anion radicals. The data do support the LSV results for AN-NO₂ and AN-CHO which suggest that the reaction order in anion radical is 2 and show that the reaction order is the same for AN-CN⁻ which could not be analyzed by LSV.

The effect of temperature on the kinetics. Conventionally, it is necessary to know the mechanism of a reaction in order to determine the activation energy. This is a consequence of the fact that activation energies are generally determined from correlations of $\log k$ vs. $(1/T)$ according to the Arrhenius equation. However, it has recently¹⁶ been shown that an analysis similar to the one described in the previous section can be applied to give apparent activation energies without the need to know either the mechanism or the rate constants. The method is based upon eqn. (10) where v_c has the same significance as before. It follows that the apparent activation energy for an electrode process

$$R_i' = f[k_{app}(1/v_c)(1/T)] \quad (10)$$

$$\ln v_c = (-E_a/R)(1/T) + c \quad (11)$$

can be obtained from eqn. (11) where c is a correlation parameter.

Apparent Arrhenius activation energies for the reactions of AN-CHO⁻ and AN-CN⁻ were obtained from the data in Table 5 using eqn. (11). The values observed, 3.2 and 4.2 kcal/mol, respectively, with correlation coefficients of 0.998 and 0.999 are clearly too low to correspond to the simple dimerization mechanism. The value of E_a obtained for AN-NO₂⁻, 0.7 kcal/mol with a correlation coefficient of 0.69, illustrates this even more dramatically. The low correlation coefficient in the latter case is a consequence of the fact that the observed

Table 5. The effect of temperature on the rate of dimerization of substituted anthracene anion radicals in DMF.^a

Substituent	Temp./°C	$v_{1/2}/V s^{-1}$
9-Nitro ^b	0.0	66
9-Nitro ^b	11.1	75
9-Nitro ^b	21.9	72
9-Cyano ^c	-0.2	46
9-Cyano ^c	8.6	60
9-Cyano ^c	21.5	82
9-Formyl ^d	0.0	68
9-Formyl ^d	9.0	80
9-Formyl ^d	22.2	105

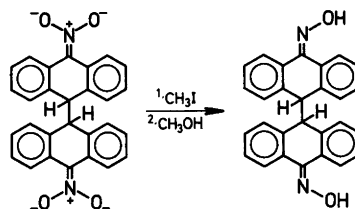
^a See Table 1 for conditions. ^b Concentration equal to 0.20 mM. ^c Concentration equal to 1.60 mM. ^d Concentration equal to 2.00 mM.

rate constant was higher at 11.1 °C than at either 0 or 21.9 °C. Unusual temperature effects observed during electrode processes has recently been attributed to complicated mechanisms.¹⁷

Electrode potentials for the reduction of substituted anthracenes. The peak potentials measured by derivative LSV at 100 V s⁻¹, where the complications due to the follow-up reactions are minimized, were observed to be -1.418, -1.646, and -1.772 V vs. Ag/Ag⁺ in acetonitrile, for the reduction of AN-NO₂, AN-CHO, and AN-CN, respectively. The solvent was DMF containing Bu₄NBF₄ (0.1 M).

DISCUSSION

The reduction of 9-substituted AN-X, where X is an electron withdrawing group, is accompanied by the formation of the corresponding dimer dianions (Scheme 1) which are stable in aprotic solvents such as DMF and acetonitrile. The structure of the dianion was established unambiguously in one case, where X=nitro, by conversion to the corresponding bianthronyldioxime¹⁸ (Scheme 2) as described in Experimental.



Scheme 2.

Although the kinetic data for the conversion of the anion radicals to the dimer dianions are consistent with rate law (7), a fact which suggests the simple dimerization mechanism, this mechanism does not fit all of the data. LSV mechanism analysis showed that the reaction order in anion radical is 2 and that for the substrate is 0. The reaction orders in anion radical were verified by DCV for all three substrates using the sweep rate tuning procedure.¹⁵ Analysis by DCV at low sweep rates revealed a minimum in the dependence of R'_i on v and the increase in R'_i with decreasing v at sweep rates lower than where the minimum was observed can only be explained by dissociation of the dimer dianions. All of the above is still consistent with the simple dimerization mechanism as long as provision for the reverse reaction is taken into account. However, there are two facts that hold for all three anion radicals that serve to rule out the simple dimerization mechanism. The first is that the DCV mechanism analysis produced slopes (eqn. 4) which are drastically different from that predicted by rate law (7). The apparent activation energies are also much lower than expected. In fact there may even be an inverse temperature effect with $\text{AN}-\text{NO}_2^-$. In any event, diffusion controlled reactions are expected to have Arrhenius activation energies of about 3–4 kcal/mol¹⁹ and the observed value for $\text{AN}-\text{NO}_2^-$ was only 0.7 kcal/mol. Since neither the DCV slopes nor the apparent activation energies are consistent with the simple dimerization mechanism, modifications in that mechanism are necessary.

Proton donors have been found to participate in a related reaction, electrohydrodimerization of activated olefins.²⁰ Although the final products in this case are not protonated, catalysis of the dimerization by proton donors cannot be ruled out from the kinetic data presented in the Tables. For this reason, voltammetry was carried out over neutral alumina which very effectively reduces the level of water to negligible concentrations.²¹ No change in the apparent rate for the reaction of $\text{AN}-\text{NO}_2^-$ could be detected upon adding alumina to the solvent–electrolyte solution. Therefore, proton donors cannot be kinetically involved in the dimer forming reactions.

Since the only species that we have been able to identify by the voltammetric and kinetic studies involved in the anion radical dimer dianion equilibria are the ions, we find no other alternative than to postulate that the reaction involves two

coupled equilibria. The first (Scheme 1) could be the formation of a complex involving two anion radicals which are not covalently bonded to each other and the second involves the reversible bond formation. The first equilibrium is necessary to account for the low apparent activation energies. It is very likely that the first equilibrium would show an inverse temperature effect. This mechanism gives rise to rate law (12) under conditions where the reverse reaction

$$\text{Rate} = [k_b k_c / (k_b + k_{-c})][\text{AN}-\text{X}^-]^2 \quad (12)$$

leading to the dimer dianion is negligible, that is at short times as in the high sweep rate experiments.

However, we now find ourselves in a dilemma. Rate law (12) is clearly identical to (7) with the appropriate substitution for k_{obs} . We have already explained that this rate law is inconsistent with the DCV mechanism analysis. Could the inconsistency be caused by the complication of the reversibility? We think not since the degree of the complication is sweep rate dependent and decreases sharply as the sweep rate is increased. Thus, if the dissociation is interfering with the DCV analysis it would be expected to give an increase in the slope (eqn. 4) rather than a decrease. Thus, we must conclude that there is some feature of the mechanism which we do not recognise, perhaps some other complicating equilibrium, which causes the DCV response to deviate from the mechanism that we show in Scheme 1. All other data that we have accumulated fit this mechanism.

In conclusion we would like to emphasize that the simple anion radical dimerization mechanism which we sought in the dimerization of $\text{AN}-\text{X}^-$ surely does not take place. There even appear to be complications beyond those that we have identified. This should serve as a further demonstration of the complexities involved in ion radical reactions as recently emphasized in other cases.^{1–3,20,22–25}

EXPERIMENTAL

Preparative electrolysis of 9-nitroanthracene. 9-Nitroanthracene (4 mmol, 0.892 g) dissolved in acetonitrile (100 ml) containing Bu_4NBF_4 (0.1 M) as supporting electrolyte was subjected to cathodic reduction at a constant current (200 mA) for 32.2 min (1 F/mol). The electrodes were platinum gauze and the cell was divided with a sintered glass disk. To the resulting solution, which showed no sign of decomposition, was added methyl iodide (5 ml)

which was accompanied by a color change from bright red to yellow. After concentration of the reaction mixture to about 5 ml, methanol (20 ml) was added followed by heating to the boiling point for 1–2 min. Cooling to room temperature was accompanied by the precipitation of a yellowish crystalline product which could be isolated by filtration. The isolated yield was 370 mg (44 %). The identity of the product, bianthronyl dioxime, was established after recrystallization from benzene–ethanol (1:3) by the melting point (292–295 °C, lit.²⁶ 297–299 °C) and the direct comparison of the IR spectrum with that of an authentic sample kindly provided by Professor J. Rigaudy.

Apparatus and procedures. The instrumentation, electrodes, cells, data handling procedures as well as solvent and electrolyte purification procedures were the same as described recently.²⁷

20. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 147.
21. Hammerich, O. and Parker, V. D. *Electrochim. Acta* 18 (1973) 537.
22. Ahlberg, E., Helgée, B. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 187.
23. Bethell, D., Galsworthy, P. J., Handoo, K. L. and Parker, V. D. *J. Chem. Soc. Chem. Commun.* (1980) 534.
24. Parker, V. D. and Bethell, D. *Acta Chem. Scand. B* 34 (1980) 617.
25. Baumberger, R. S. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 537.
26. Rigaudy, J., Barcelo, J. and Raubaud, M. *Bull. Soc. Chim. Fr.* (1969) 3538.
27. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 97.

Received February 12, 1981.

REFERENCES

1. Aalstad, B., Ronlán, A. and Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 247.
2. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 149.
3. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 279.
4. Steckhan, E. *J. Am. Chem. Soc.* 100 (1978) 3526.
5. Burgbacher, B. and Schäfer, H. *J. Am. Chem. Soc.* 101 (1979) 7590.
6. Childs, W. V., Maloy, J. T., Keszthelyi, C. P. and Bard, A. J. *J. Electrochem. Soc.* 118 (1971) 874.
7. Hazelrig, M. T. and Bard, A. J. *J. Electrochem. Soc.* 122 (1975) 211.
8. Bard, A. J., Puglisi, J. V., Kenkel, J. V. and Lomaz, A. *J. Chem. Soc. Faraday Discuss.* 56 (1973) 353.
9. Lamy, E., Nadjó, L. and Savéant, J. M. *J. Electroanal. Chem.* 50 (1974) 141.
10. Bezilla, B. M., Jr. and Maloy, J. T. *J. Electrochem. Soc.* 126 (1979) 579.
11. Hammerich, O. *The Third EUCHEM Meeting on Organic Electrochemistry*, Pitlochry, Scotland, May 23–27, 1977.
12. Yildiz, A. and Baumgärtel, H. *Ber. Buns. Ges.* 81 (1977) 1177.
13. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 117.
14. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 259.
15. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 233.
16. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 51.
17. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 123.
18. Nielsen, A. T. In Feuer, H., Ed., *The Chemistry of the Nitro and Nitroso Groups*, Interscience, New York 1969, p. 349.
19. Caldin, E. F. *Fast Reactions in Solution*, Oxford Univ. Press, London-New York 1964.